

HETEROCYCLIC-FUSED TROPYLIUM IONS SYNTHESIS AND STABILITY

Peter Pedaja



LUND 1982



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SYNTHESIS AND STABILITY

Peter Pedaja, fil. kand., Klm

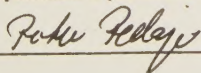
Lund 1982

Organization LUND UNIVERSITY Division of Organic Chemistry 1 Chemical Center P.O. Box 740 S-220 07 Lund		Document name DOCTORAL DISSERTATION	
		Date of issue April 1982	
Author(s) Peter Pedaja		CODEN: LUNKDL/(NKOK-1009)/1-25 / (1982) Sponsoring organization	
Title and subtitle HETEROCYCLIC-FUSED TROPYLIUM IONS SYNTHESIS AND STABILITY			
Abstract The syntheses of the following annelated cycloheptatrienes are described: 4H-cyclohepta[2,1-b;3,4-b']dithiophene, 4H-cyclohepta[1,2-b;4,3-b']dithiophene, 4H-cyclohepta[1,2-c;3,4-c']dithiophene(I), 10H-benzo[4,5]cyclohepta[2,1-b]thiophene, 10H-benzo[4,5]cyclohepta[2,1-b]selenophene and 10H-benzo[4,5]cyclohepta[2,1-b]furan(II). Treatment of these compounds with triphenylmethyl tetrafluoroborate gave the following heterocyclic fused tropylium ions: 4H-dithieno[2,1-b;3,4-b']tropylium fluoborate, 4H-dithieno[1,2-b;4,3-b']tropylium fluoborate, 10H-benzo[4,5]thienol[2,1-b]tropylium fluoborate and 10H-benzo[4,5]selenol[2,1-b]tropylium fluoborate. pK_p^+ values of these ions, determined by potentiometric titration, were found to be 5.6, 6.0, 3.8 and 3.4, respectively. From (I) and (II) the corresponding ions could not be obtained. The stabilities are discussed and compared to other fused tropylium ions. Preparations of the cycloheptatriene systems were made by two different routes. Thus, the cycloheptadithiophenes were obtained by coupling of methylthienyl lithium by copper(II) chloride to give dimethyl-bithienyls, which were side chain brominated with N-bromosuccinimide to give bis-bromomethyl bithienyls. Ring closure to the seven-membered ring was achieved by reaction with diethyl malonate anion. Hydrolysis and thermal decarboxylation then gave the monocarboxylic acid. This was converted to quaternary ammonium salt, which after elimination gave the cycloheptatrienes. Direct one-step elimination was achieved in one case by lead tetraacetate promoted oxidative decarboxylation. The benzocyclohepta fused heterocycles were prepared by Wittig reaction of o-carboxybenzyl triphenyl phosphonium bromide methyl ester with the appropriate 3-formyl heterocycle. The Z-isomer was obtained after distillation. Diisopropylamide mediated ring closure gave the tricyclic ketones. Reduction with lithium aluminium hydride/aluminium chloride gave the benzo heterocyclic fused cycloheptatrienes.			
Key words			
Classification system and/or index terms (if any)			
Supplementary bibliographical information			Language English
ISSN and key title			ISBN
Recipient's notes		Number of pages 25	Price
		Security classification	

Distribution by (name and address) **Peter Pedaja, Division of Organic Chemistry 1, Chemical Center, P.O. Box 740, S-220 07 Lund, Sweden**

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Date 1982-04-01

This review is a summary of the following papers,
referred to as I-VI.

- I. S. Gronowitz, P. Pedaja
Heterocyclic-fused tropylium ions VI
Syntheses and stability of 4H-dithieno[2,1-b;3,4-b']-
tropylium fluoroborate and 4H-dithieno[1,2-b;4,3-b']-
tropylium fluoroborate.
Tetrahedron 34, 587 (1978)
- II. S. Gronowitz, P. Pedaja
The reaction of some 2-thienyllithium derivatives with
some alkyl tosylates.
Chemica Scripta 15, 187 (1980)
- III. A. Hallberg, S. Liljefors, P. Pedaja
A simplified synthesis of 3-bromoselenophene and
some 3-bromothiophenes.
Synthetic Communications 11(1), 25 (1981)
- IV. P. Pedaja, S. Gronowitz
Heterocyclic-fused tropylium ions VIII
The synthesis of 4H-cyclohepta[1,2-c;3,4-c']dithiophene
and its reaction with triphenylmethyl tetrafluoroborate.
Chemica Scripta, accepted for publication
- V. A. Hallberg, P. Pedaja
A novel synthesis of some tricyclic ketones via lithium-
diisopropylamide mediated cyclization.
To be published
- VI. P. Pedaja, S. Gronowitz
Heterocyclic-fused tropylium ions IX
Synthesis and stability of benzo[4,5]thieno[2,1-b]-,
benzo[4,5]furano[2,1-b]-, and benzo[4,5]selenolo[2,1-b]-
tropylium tetrafluoroborate.
To be published

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1. INTRODUCTION

The tropylium ion, first prepared by Merling in 1891,¹ was not recognized as such until 1954, when von Doering and Know, encouraged by Hückel's theory of aromaticity, repeated Merling's experiment.² They also determined the stability of the tropylium ion by means of its acidity constant, and found it to equal that of acetic acid, 4.7. Since then, a variety of substituted tropylium ions has been prepared, their stabilities investigated and rationalized. Review articles have been published covering the subject.³⁻⁵

It has been found that electron-donating substituents stabilize the ion, whereas electron acceptors have a destabilizing effect. Condensed tropylium ions, on the other hand, present a somewhat more complex behaviour. Benzene annelation lowers the stability, although one could expect the opposite due to possible delocalization of charge. Thiophene annelation, on the other hand, increases the stability of the ion. This difference between benzene and thiophene annelation has been explained by assuming that the benzene ring stabilizes the uncharged cycloheptatriene system more than the tropylium ion,⁴ whereas in the thiophene case the opposite is true. Also, it has been pointed out that annelation of a five-membered ring, such as thiophene, onto a seven membered ring, will cause less angular strain than annelation of a six membered benzene ring.⁷ This has been confirmed by X-ray investigations.⁸ Furthermore, it has been pointed out that a thenylic position stabilizes a positive charge better than a benzylic position does.⁷

Annelation of additional benzene rings further lowers the stability of the ion due to, in some isomers, steric hindrance and breakdown of planarity.⁶ Annelation of an additional thiophene ring to a thienotropylium ion, on the other hand, has only a minor influence on the stability.⁷

Two dithienotropylium ions, as well as a corresponding tropone has been subjected to X-ray investigations, and have been found to be almost planar.⁸⁻¹⁰ Dibenzotropone, on the other hand, has been found to be non-planar.¹¹ The tropylium ions corresponding to cycloheptadithiophenes 1 and 2 were considered to be of interest with respect to possible peri effects between thiophene hydrogens. In 1 no such effect is to be expected, whereas in 2 interaction might cause a lowering of the stability of the corresponding ion.

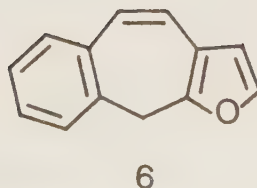
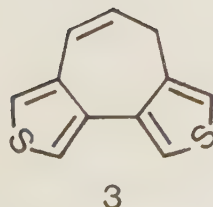
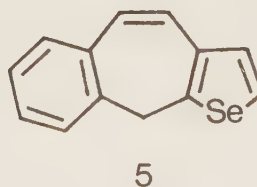
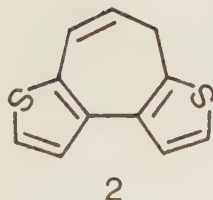
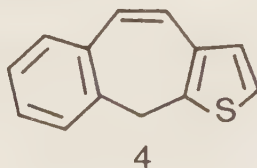
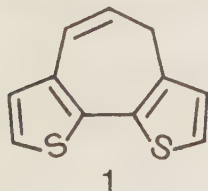
In order to rationalize the different stabilities and to make possible predictions about new tropylium ions, a topological approach has been applied by Gutman and Trinajstić.¹² Heterocyclic fused systems are considered mainly by the topology of the parent hydrocarbon after removal of the heteroatom. The stabilities are then rationalized by regarding the type of ring branching present. Thus, it has been suggested that c-annulation of heterocyclic rings will lower the stability, and also that the type of heteroatom present is of minor importance. The tropylium ions corresponding to cycloheptatrienes 3-6 were considered to be of interest to appreciate the value of this theoretical approach.

The present work was initiated by Professor Gronowitz and constitutes a continuation of investigations of heterocyclic-fused tropylium ions made at this department since the late sixties.¹³⁻¹⁴

2. SYNTHESIS

A variety of methods exists for the preparation of tropylium ions,⁴ the most common ones being hydride ion abstraction from the corresponding hydrocarbon or dissociation of carbinols in acid solution. Throughout this work, the hydride ion abstraction method has been employed, using triphenylmethyl tetrafluoroborate as hydride ion acceptor.

The tropylium ion precursors 1-6 have been synthesized, and their preparations will be discussed separately. Chapter 2.1 deals with the cycloheptadithiophenes and chapter 2.2 with the benzocyclohepta fused heterocycles.



2.1 Cycloheptadithiophenes

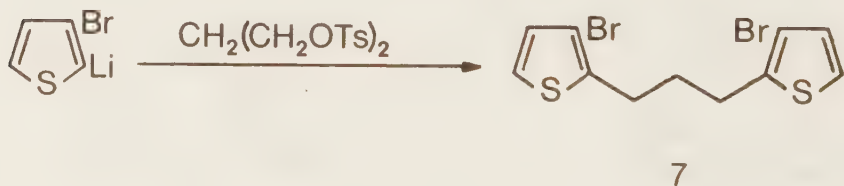
2.1.1 Simple starting materials

Ortho-bromo-methylthiophenes have been used in rather large amounts throughout this work, and have been prepared by the method described in paper III, with the exception of 2-bromo-3-methylthiophene, which was prepared according to a literature method.¹⁵

The appropriate methylthiophene was thus brominated in aqueous sodium acetate to the di- or tri-bromo derivative. The hydrogen bromide formed was neutralized by the acetate, thereby producing acetic acid in an amount suitable for the subsequent reduction by zinc. Intermediate work-up of the di- or tri-bromo compound is not necessary, resulting in a convenient one-pot procedure.

Bis-bromomethyl-bithienyls were prepared by radical bromination of the appropriate dimethyl-bithienyls with N-bromo succinimide in carbon tetrachloride.

The dithienopropane 7 was obtained by reaction of 3-bromo-2-thienyllithium with 1,3-propandiol ditosylate.

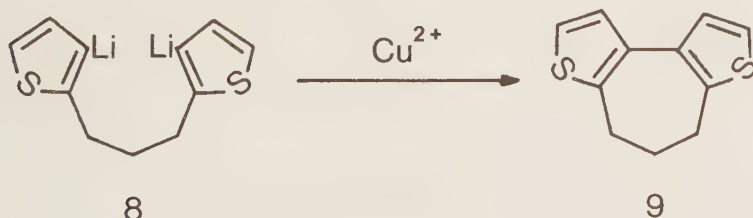


This reaction, as well as other reactions of thienyllithiums with different alkyl tosylates, is reported in paper II. In summary, these investigations showed that alkyl tosylates can be used to alkylate thienyllithium derivatives, provided a bulky substituent (bromo or methyl) is present in the position ortho to the lithium. Otherwise, the corresponding sulphone is obtained. Methyl tosylate, however, gives alkylation of thienyllithium independent of the nature of the ortho-substituent.

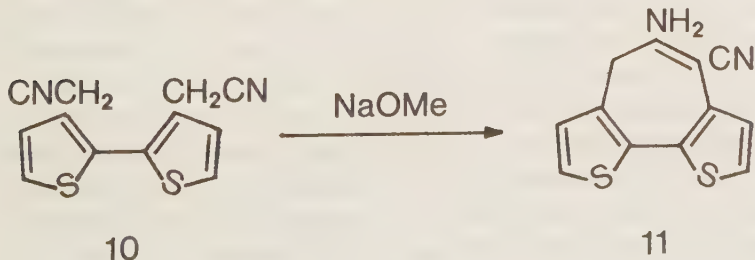
2.1.2 Ring-forming reactions

There are two main synthetic approaches to the cyclohepta-dithiophene systems. Either one can start from suitably substituted thiophenes and then make the seven-membered ring, or one can apply thiophene-forming reactions on a functionalized seven-membered ring. Since suitably substituted thiophenes can be readily obtained, and seven-membered rings are easily formed, the former approach was considered more convenient.

Formation of the seven-membered ring was achieved in three different ways. The first method, reported in paper II, utilizes the copper(II) promoted coupling of thienyllithium as the ring-forming step. However, this method gave only a low yield of compound 9, and furthermore, introduction of the double bond could not be made in an acceptable yield.

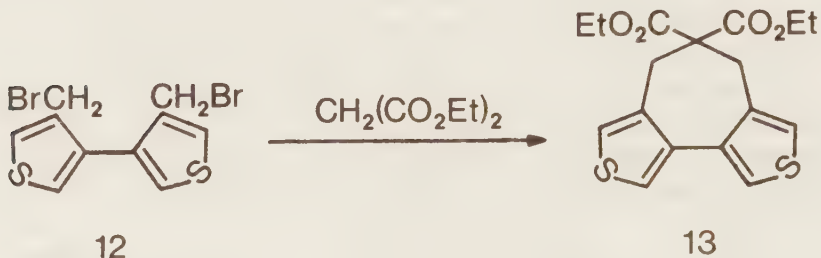


The Thorpe-Ziegler cyclization is known to give seven-membered rings in good yields,¹⁶ and was therefore applied to the bis-cyanomethyl-bithienyl 10. This is reported in paper I.



However, the enamino nitrile 11 could not be converted to the cycloheptadithiophene 1, and therefore this method was not further explored.

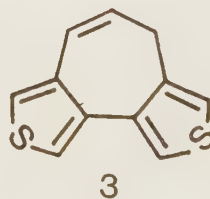
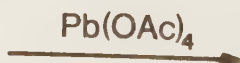
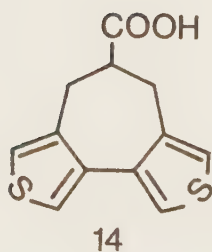
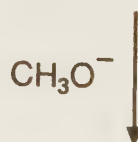
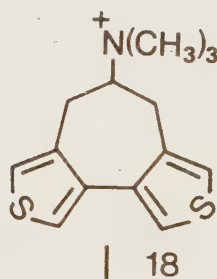
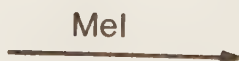
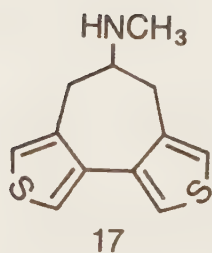
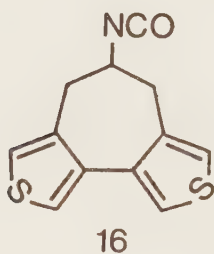
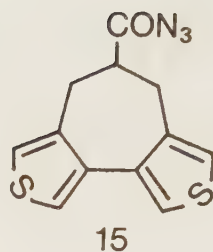
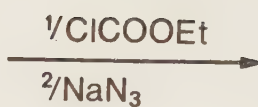
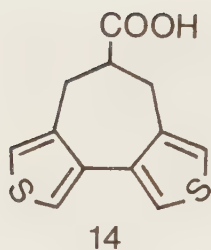
Dialkylation of diethyl malonate with bis-bromomethyl-bithienyl proved to be the most fruitful approach to the required cycloheptadithiophene systems, and is exemplified below for one of the isomers. This method is reported in papers I and IV.



2.1.3 Introduction of the double bond

The functional group manipulations required to obtain the cycloheptadithiophenes 1-3, from the diester 13 and its isomers, followed two routes, both starting with hydrolysis and decarboxylation to give the monocarboxylic acids. The first method, applicable to all three isomers, consisted of transforming the carboxy function to a readily eliminated, quaternary ammonium group. This was achieved via initial transformation to the corresponding acyl azides, followed by a Curtius rearrangement giving the isocyanates, and subsequent reduction to the methyl amines. Exhaustive alkylation then gave the required cycloheptadithiophenes 1-3. This method, exemplified on page 12 for one of the isomers, is reported in papers I and IV.

The second, simpler method, which was useful only in the case of the c,c-annelated isomer, utilized the oxidative decarboxylation of the monacid 14 with lead tetraacetate to give the cycloheptadithiophene 3 directly in a one-step reaction. This second method is reported in paper IV.



2.2 Benzocyclohepta fused heterocycles

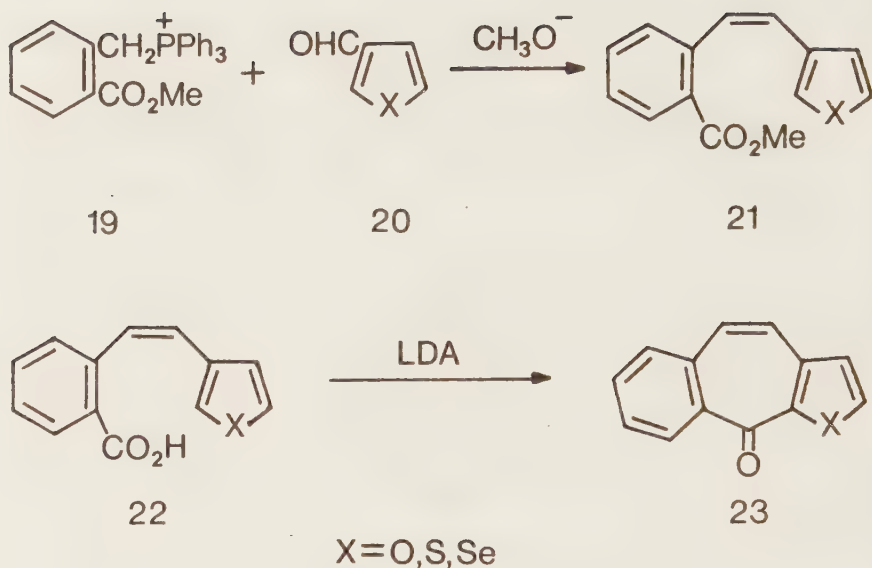
Several papers have been published on the synthesis of the thiophene system and its derivatives and isomers,¹⁷⁻²⁰ although the benzocycloheptathiophene 4 was only obtained unintentionally.¹⁷

The synthetic approach to this system has, in most cases, been a Wadsworth-Horner modification of the Wittig reaction between a suitable o-formyl benzoic acid and different thenylphosphonates. The resulting olefin, mainly in its E-configuration, has then been hydrogenated prior to the ring closure in polyphosphoric acid. Ring closure via the acid chloride has also been frequently used. The double bond, when required, has then been reintroduced by means of a bromination-dehydrobromination sequence.

It was considered more convenient to prepare the olefin in its Z-configuration, and then perform the ring closure, which could be expected to proceed in even better yields than from the saturated isomer.

The Wadsworth-Horner reaction is known to give olefins mainly in their E-configuration,²¹ although exceptions have been reported.²² The normal Wittig reaction, on the other hand, often gives the Z-isomer in high yields.²³ A recent publication reports a modification using diphenylalkyl phosphonoxides, which gives the Z- or E-isomer specifically.²⁴ Also, a convenient two-phase reaction giving good ratios of the Z-isomer has been reported.²⁵

Taking into account the required starting materials, it was found that the most convenient access to the Z-isomers was via reaction of the 3-formyl heterocycles 20, with o-carboxybenzyltriphenylphosphonium bromide methyl ester, 19. The Z/E ratio was found to be 70/30 in the case of the thiophene and selenophene isomers, whereas it was 50/50 when the heterocycle was furan. Separation of the isomers was easily achieved by distillation or, in the case of selenophene, by their different solubilities in hexane. The Z-acids 22 were then obtained after hydrolysis with aqueous sodium hydroxide.



Quite surprisingly, the ring closure to the tricyclic ketones gave only low yields when the common polyphosphoric acid method, as well as the acid chloride method, was applied. A Parham-type cycliacylation²⁶ was considered as a possible alternative to obtain the required ketones. Therefore, 22 was treated with lithium diisopropylamide (LDA), which gave the expected ketones 23 in 40-65 % yield.

Obviously, lithiation occurs to a large extent in the 2-position of the heterocyclic ring. The reason for this positional preference could be either the weak electron-withdrawing effect of the double bond, or a directing effect of the suitably positioned carboxy function. In compound 24, where none of these effects is expected, lithiation has been reported to occur in the 2- and 5-positions of the thiophene ring in a ratio of 17 to 83.²⁷



24

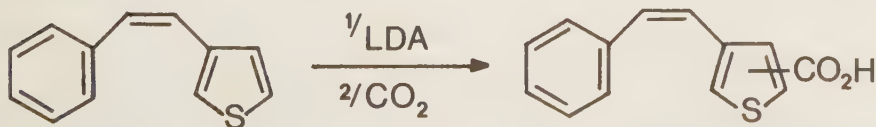
If it is assumed that the carboxy function in 22 directs lithiation to the 2-position of the thiophene ring, the same effect could also be expected in lithiation of 25, although less pronounced due to the higher flexibility of this system.



25

26

It was found, however, that ketone 26 was formed in a yield of only 12 %. Obviously, directed metalation by the carboxy function is not involved in this system. Lithiation of compound 27, on the other hand, gives, after carbonation, a mixture of two acids in a 50/50 ratio. According to mass spectra these were isomeric monoacids, and are assumed to be the 2- and 5-isomers of 28.



27

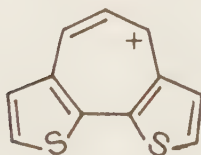
28

It can therefore be concluded that in the lithiation of 22 the position of metalation depends only on the presence of the double bond and not on the carboxy function. The fact that a yield higher than 50 % was obtained in this case can be accounted for by assuming a transmetalation from the 5- to the 2-position of the thiophene ring. These reactions are reported in paper V.

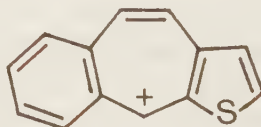
The required cycloheptatrienes 4-6 were then obtained by reduction of the corresponding ketones with lithium aluminium hydride/aluminium chloride, as reported in paper VI.

2.3 Preparation of tropylium ions

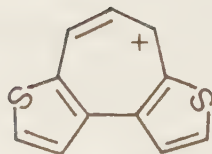
The tropylium ions were all prepared by hydride ion abstraction from the corresponding cycloheptatrienes by treatment with triphenylmethyl tetrafluoroborate in acetonitrile/ethyl acetate solutions. In most cases, the tropylium ions precipitated within a few minutes after addition of the hydride ion acceptor. In this way the following four tropylium ions were prepared:



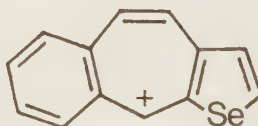
29



30



31



32

All ions were obtained as high melting, stable crystals, which could be stored with no special precautions.

From two of the cycloheptatriene systems, the expected ions could not be isolated. Thus, the benzofuro tropylium ion, which was identified by NMR only, was formed in a small amount together with an unidentified product. Possibly the high reactivity of the furan ring causes reaction with the triphenylmethyl cation. Nitrosonium hexafluorophosphate²⁸ was used in a subsequent experiment, but the same result was obtained as when the triphenylmethyl cation was used. However, these results are somewhat unexpected since both the furo tropylium ion²⁹ and two furo-thieno tropylium ions⁷ have been found to be very stable. Furthermore, the selenophene and thiophene analogues were readily obtained, although these are expected to be less stable than the benzo-furo tropylium ion.

Not that surprising, however, is the fact that the dithieno(c,c) annelated tropylium ion corresponding to cycloheptadithiophene 3 could not be obtained. Several unsuccessful attempts to prepare thieno(c) annelated tropylium ions have previously been reported.^{30,14} This will be further discussed in chapter 3.

3. STABILITY OF TROPYLIUM IONS

3.1 Determination of stability

The stability of a tropylium ion is often discussed in terms of its acidity constant K , according to the following equations:

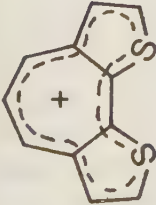


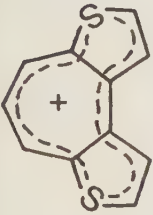
$$K = \frac{(ROH)}{(R^+)} \frac{(H_3O^+)}{(H_2O)^2} \quad (2)$$

$$pK = pH - \log \frac{(ROH)}{(R^+)} \quad (3)$$

Titration of dilute aqueous solutions of the cation with base will produce f -shaped titration curves like those obtained from the titration of ordinary weak acids. From equation (3) it follows that the pK -value is equal to the pH -value when the concentration of the conjugate base, ROH , equals that of the cation, R^+ . Thus, the pK -value is obtained from the titration curve and equals the pH -value at half the neutralization point. As these constants refer to cations they will be denoted pK_R^+ -values. A high stability of the cation will result in a low concentration of hydronium ion, and consequently in a high pK -value.

The four tropylium ions described in chapter 2 were all titrated with base and gave titration curves as expected for weak acids. It should however be pointed out that in some cases solubility problems were encountered. The pK_R^+ -values obtained were between 3.4-6.0, and are reported on page 19 together with the pK_R^+ -values of some previously reported tropylium ions.

No.	pK _R ⁺ Ref.	
29		5.6
30		3.8
		4.7
		6.0
33		6.6

No.	pK _R ⁺ Ref.	
31		6.0
32		3.4
		1.7
		6.9
34		5.4
		35
		29
		36

3.2 Discussion

A peri-effect between the thiophene hydrogens in 31 would cause a breakdown of planarity and thus a lowering of the stability as compared to 29.

Obviously, no pronounced peri-effect between the thiophene hydrogens can be present in 31 since the stability of this ion is even greater than that of 29. The difference of 1.2 pK_R^+ units found between ions 33 and 34 can be explained by the fact that in 33 the positive charge can be mainly localized at the 2-thenylic position, whereas in 34 the charge will be found mainly at the less favourable 3-thenylic position. In 32 it is reasonable to assume that the positive charge is mainly located at the 2-thenylic position and in 29 at the 3-thenylic position. Thus, a difference in stabilities similar to that between 33 and 34 would be also expected in this case. As can be seen, however, the difference is only 0.4 pK_R^- units compared to 1.2 between 33 and 34. This lower than expected stability of 31 can possibly be attributed to a small peri-effect between the thiophene hydrogens.

The thieno[c,cltropylium ion corresponding to cycloheptadithiophene 3 could not be prepared, or even detected in solution. This is not totally unexpected, since it has been reported that the c,c-annelated isomer of 33 could not be prepared.¹⁴ Also, attempted preparation of 2,5-dimethyl thieno[cltropylium has been unsuccessful.³⁰ However, a few methyl substituted c- and c,c-annelated thienotropylium ions have been reported.³¹⁻³³ Although in no case has the pK_R^+ value been reported, it has been shown in one case that the stability of the thieno[c] annelated ion is considerably lower than that of the tropylium ion.³³ These results are in complete agreement with the topological approach of Gutman and Trinajstić,¹² according to which c-annelation is expected to cause a considerable lowering of the stability.

It is seen from the values reported on page 19 that the stabilities of ions 30 and 32 are lower than that of tropylium

itself but somewhat higher than that of benzo tropylium. Obviously, the destabilizing effect of benzo-annulation is not fully compensated for by the stabilizing effect of thiophene. The somewhat lower stability of 32 as compared to 30 is in agreement with the predictions of the topological approach, which suggests that the influence of the heterocycle, in heterocyclic fused tropylium ions, will decrease as the size of the heteroatom and the carbon-heteroatom bond length increase. Thus, the tropylium ion will become more like the non-hetero annelated analogue, in this case benzo tropylium, with pK_R^+ -value 1.7.

Of the heterocyclic fused tropylium ions, thieno[b]-tropylium has been known since 1963,³⁴ whereas furo[b]tropylium was not reported until 1980.²⁹ Selenolo[b]tropylium has not yet been reported, but considering the stability of 32 it can be expected to be slightly less stable than thieno tropylium. Thus, it can be concluded that the type of heteroatom in heterocyclic b-fused tropylium ions is of minor importance for the stability.

It has been pointed out that a relative estimation of the stability of tropylium ions can be made by regarding the IR absorption frequencies of the corresponding tropones,¹⁴ because the carbonyl bond will be more or less polarized depending on the degree to which the positive charge can be delocalized. A high degree of polarization will result in a lowering of the absorption frequency as compared to the unpolarized bond. The IR carbonyl frequencies of the tropones corresponding to ions 33 and 34 are 1545 and 1568 cm^{-1} , respectively, whereas dibenzotropone absorbs at 1650 cm^{-1} . The pK_R^+ -values are 6.6, 5.4 and -1.9, respectively.⁷ Thus it can be seen that, as expected, a lower carbonyl frequency corresponds to a higher pK_R^+ -value.

The carbonyl frequencies of the tropones corresponding to 30 and 32 are 1560 and 1540 cm^{-1} , respectively, which implies pK_R^+ -values similar to those of 33 and 34, whereas the observed values are only 3.8 and 3.4. If the differences in carbonyl frequencies between the tropones and the saturated ketones are compared, instead of the absolute values, the same result is

obtained. Therefore, it can be concluded that this type of estimation of stabilities of tropylium ions should be used to make only very rough estimations of pK_R^+ -values.

To summarize the results of this work with what is previously known about annelated tropylium ions, it can be stated that there are only minor differences in the stabilities of the different heteroaromatic b-annelated tropylium ions. Also, the stability decreases as the size of the heteroatom increases.

Dithieno[b,b] annelated ions vary only slightly in stability with the mode of annelation, and their stabilities are similar to that of thieno[b]tropylium, whereas c- and c,c'-annelated thieno and dithieno tropylium ions are considerably less stable.

The destabilizing effect of benzo annelation cannot be fully compensated for by simultaneous annelation of thiophene or selenophene.

ACKNOWLEDGEMENT

I would like to express my sincere thanks to all those who have assisted me in the completion of this work.

Financial support has been obtained from the Swedish Natural Science Research Council (to Salo Gronowitz), the Faculty of Science, University of Lund and from the Royal Physiographic Society of Lund.

REFERENCES

1. G. Merling, Ber. 3108 (1891)
2. W. von Doering, L.H. Knox, J. Am. Chem. Soc. 76, 3203 (1954)
3. M.E. Vol'pin, Russ. Chem. Rev. 29, 129 (1960)
4. G.D. Kolomnikova, Z.N. Parnes, Russ. Chem. Rev. 36, 735 (1967)
5. F. Pietra, Chemical Reviews 73, 293 (1973)
6. D. Meuche, H. Strauss, E. Heilbronner, Helv. Chim. Acta 41, 414 (1958)
7. S. Gronowitz, B. Yom-Tov, U. Michael, Acta Chem. Scand. 27, 2257 (1973)
8. J.-E. Andersson, Acta Cryst. 34, 2235 (1978)
9. J.-E. Andersson, Ibid. 35, 1349 (1979)
10. J.-E. Andersson, Ibid. 37, 401 (1981)
11. H. Shimanouchi, T. Hata, Y. Sasada, Tetrahedron Letters 3573 (1968)
12. I. Gutman, N. Trinajstić, Croat. Chem. Acta 46, 243 (1974)
13. U. Michael, Thesis, Lund 1971
14. B. Yom-Tov, Thesis, Lund 1972
15. A. Wiersema, S. Gronowitz, Acta Chem. Scand. 24, 2593 (1970)
16. E.C. Taylor, A. McKillop, The Chemistry of o-Aminonitriles. Wiley, New York (1970)
17. M. Rajšner, J. Metyšová, M. Protiva, Coll. Czech. Chem. Commun. 34, 468 (1969)
18. J.M. Bastian, A. Ebnöther, E. Jucker, E. Rissi, A.P. Stoll, Helv. Chim. Acta 54, 277 (1971)
19. L. Svensson, Thesis, Lund 1979
20. J.M. Bastian, A. Ebnöther, E. Jucker, E. Rissi, A.P. Stoll, Helv. Chim. Acta 49, 214 (1966)
21. D.H. Wadsworth, O.E. Shupp, III, E.J. Seus, J.A. Ford, Jr., J. Org. Chem. 30, 680 (1965)
22. B. Yom-Tov, S. Gronowitz, Chem. Scripta 3, 37 (1973)
23. B. Yom-Tov, S. Gronowitz, Ibid. 3, 165 (1973)
24. A. Buss, S. Warren, Chem. Commun. 100 (1981)

25. G. Märkl, A. Mertz, *Synthesis* 295 (1973)
26. D. Reames, D. Hunt, C.K. Bradsher, *Synthesis* 457 (1980)
27. S. Gronowitz, K. Stenhammar, L. Svensson,
 Heterocycles 15, 947 (1981)
28. G. Olah, G. Salem, J. Staral, T.-L. Ho,
 J. Org. Chem. 43, 173 (1978)
29. M. Kato, H. Kobayashi, T. Miwa,
 Tetrahedron Letters 21, 3375 (1980)
30. D.N. Nicolaides, C.N. Coutrakis, *Synthesis* 268 (1977)
32. T. Brown, W. Carruthers, *J. Chem. Soc., Perkin Trans 1*
 2904 (1981)
32. R. Guillard, P. Fournari, *Bull. Soc. Chim.* 1437 (1971)
33. A.V. Eltsov, A.A. Ginesina, *Zhur. Org. Khim.* 3(1), 191
 (1967)
34. D. Sullivan, R. Pettit, *Tetrahedron Letters* 401 (1963)
35. G. Naville, H. Strauss, E. Heilbronner,
 Helv. Chim. Acta 43, 1221 (1960)
36. S. Gronowitz, B. Yom-Tov, *Z. Chemie* 10, 389 (1970)

